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# The Trapping of Noble Gases in Interstellar Ice Residues

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## Introduction

One of the enduring mysteries in the field of noble gas analyses of terrestrial and extraterrestrial materials is the origin of three basic noble gas components (see review by Swindle, 1988). It has been more than three decades since the discovery that the elemental abundance pattern of noble gases in most chondrites differs from either the solar or terrestrial patterns, which in turn differ from each other, and that there are also some isotopic differences, particularly in the terrestrial pattern. Although there has been considerable progress on some aspects of the problem, there is still no consensus about how and where the chondritic (historically known by the misnomer "planetary") and terrestrial patterns were produced.

There are several properties of the chondritic noble gases that have to be explained by any model for their origin:

- 1) The primary carrier is carbonaceous.
- 2) Compared to solar abundances, the gases are progressively less depleted with increasing atomic mass. In other words, the Xe/Ar ratio is much higher in chondritic noble gases than in the solar wind.
- 3) The gases are sited near the surfaces of grains, but are not released (during stepwise heatings) until temperatures of 1000°C or more.
- 4) The noble gases are relatively abundant: carbonaceous residues typically contain roughly  $3 \times 10^{-7}$  cm<sup>3</sup>STP/g each of <sup>132</sup>Xe and <sup>84</sup>Kr (e.g., Ott et al., 1981), corresponding to a distribution coefficient for Xe of  $3 \times 10^4$  cm<sup>3</sup>STP/g/atm, assuming that incorporation occurs in the solar nebula, with a total nebular pressure of  $10^{-4}$  atm.
- 5) There is little or no isotopic fractionation relative to the solar wind, but there does seem to be a contribution at some isotopes from components carried in interstellar diamonds. This is in sharp contrast to terrestrial and martian noble gases, which have noticeably isotopic fractionations in Ne and Xe.

Explaining all of these properties simultaneously has proven difficult. Because of property 1), attention has naturally focussed on carbonaceous materials. A number of processes can account for the relative elemental abundance pattern (property 2), at least qualitatively. These include adsorption, incorporation into silicate grains with icy mantles, and others. However, most models fail to reproduce the siting (property 3), the most notable exception being the models devised by the University of Chicago lab (Wacker, 1989; and references therein). In the Chicago model, noble gases either become lost in near-surface labyrinths from which they cannot escape diffusively, or else they diffuse in through pores that then shrink, blocking the path of retreat.

Most experiments have failed to reproduce the absolute elemental abundances of the heavy gases (property 4). Even when the amount of Xe in the carbonaceous material is as high as that in the carbonaceous residues from chondrites (e.g., Wacker et al., 1985), this has usually been produced by exposing the experimental sample to many orders of magnitude higher partial pressures of Xe than would be expected in nature in the process being simulated (i.e., the distribution coefficients are far too low). The notable exception is a set of experiments by Nichols et al. (1992). In those experiments, silicate "smokes" were exposed (at 10 K) to noble gases and/or a methane-ammonia-water mixture and were then irradiated with 1 MeV protons. Some of those experiments did achieve the required abundance and distribution

coefficient for Xe, but the Xe/Ar fractionation was far higher than observed in meteorites and they observed more isotopic fractionation than can be comfortably accommodated in models of chondritic noble gases. A crucial difference between the experiments of Nichols et al. (1992) and most others is that Nichols et al. assumed an interstellar cloud environment, rather than the solar nebula environment favored by the Chicago group and many others.

Most of the material in interstellar space is concentrated in large molecular clouds. At the low temperatures characteristic of these environments ( $T = 10-40$  K), most gas phase species, including many of the noble gases, will condense out onto grains in the form of mixed-molecular ices (see Sandford & Allamandola, 1993; and references therein). Infrared spectroscopy of protostars embedded in these clouds shows that these icy grain mantles consist largely of simple molecules like  $H_2O$ ,  $CH_3OH$ ,  $CO$ ,  $NH_3$ ,  $H_2$ , and perhaps  $CO_2$  and  $CH_4$  (cf. Allamandola & Sandford, 1988; Allamandola et al., 1992; Sandford et al., 1993). In addition, cosmic rays and attenuated ultraviolet (UV) radiation within interstellar clouds provides enough energy to produce more complex species through the irradiation of the molecules in the grain mantles. Warming of these irradiated ices results in the production of more complex molecular species (cf. Allamandola et al., 1988; Bernstein et al., 1995). Evidence for such species has been found in a number of interstellar spectra (cf. Tegler et al., 1993).

As part of an ongoing research program under the Origins of Solar Systems (OSS) Program, the research group at NASA/Ames, of which Scott Sandford is a co-leader, has been studying the properties of interstellar and cometary ice analogs in the laboratory. It has been found that UV photolysis and thermal processing of ice analogs containing  $H_2O$ ,  $CH_3OH$ ,  $CO$ , and  $NH_3$  results in the production of relatively complex organic residues (Allamandola et al., 1988; Bernstein et al., 1995). Work done at NASA/Ames in the past few years has produced excellent spectroscopic evidence that the infrared spectra of these residues provide a good match to those of the organic component of the diffuse interstellar medium (Sandford et al., 1991; Pendleton et al., 1994).

Since our Solar System is thought to have formed from an accretion disk (the solar nebula) derived from the collapse of a portion of an interstellar cloud, the raw material in the disk presumably contained the diverse states of molecular complexity which were present in the parent cloud. The infalling material would have been modified to varying extent by a number of chemical and physical processes during the cloud collapse and accretion shock. Ultimately, at least some of this material, whether altered in the nebula or accepted unchanged from the interstellar medium, became incorporated into asteroids, the presumed parent bodies of meteorites. Thus, it is perhaps not surprising that the spectra of the refractory organic residue produced from the laboratory interstellar ice analogs also reproduce many of the features seen in spectra of the acid insoluble carbonaceous component of meteorites (Pendleton et al., 1994).

The possibility that the chondritic noble gas component might be related to processes occurring in interstellar clouds, and hence that the high distribution coefficient required of nebular processes is not necessary, is the primary motivation for this work. At the dust temperatures typical of dense interstellar clouds ( $10 - 40$  K) most molecular and atomic species will condense onto grains, the major exceptions being H, He, and to a lesser extent Ne,  $H_2$ , and  $CO$ , which will only partially condense. Thus, an elemental fractionation of the noble gases like that of the chondritic gases, i.e. relatively large amounts of Ar, Kr, and Xe with minor amounts of Ne and little or no He, would be a natural consequence of condensation processes in the interstellar cloud that ultimately formed our solar system. The distribution of noble gases condensed in this manner may then be 'fixed' onto the

interstellar grains by trapping into a carbonaceous carrier phase produced during subsequent irradiation of the noble gas-containing ice.

The Ames group's experiments on analogues of interstellar and cometary ices (Allamandola et al., 1988; Bernstein et al., 1995) usually include repeated cycles of deposition of a mixture of gases (e.g.,  $\text{H}_2\text{O}+\text{CH}_3\text{OH}+\text{NH}_3+\text{CO}$ ) onto a cold (e.g., 10 K) substrate, followed by ultraviolet irradiation. Finally, the sample is warmed to room temperature. This process produces a variety of new, complex molecular species, many of which are refractory enough to survive as a solid at 300 K (Allamandola et al., 1988; Bernstein et al., 1995). This group has recently expanded their studies to include ices that also contain polycyclic aromatic hydrocarbons (PAHs). PAHs, which have been identified as an abundant form of carbon in the interstellar medium (Allamandola et al., 1989), consist of co-joined, planar, 6-membered carbon rings having hydrogen on their peripheries. PAHs are relatively refractory molecules and in dense molecular cloud environments they should be efficiently frozen out onto grains along with other molecular species. Once incorporated into the ices, they may participate in any subsequent irradiation chemistry and become bound into the resulting organic residue that survives to room temperature. The interlinking of PAHs into the residue would likely result in materials very similar to meteoritic kerogens, which are rich in aromatics. The Ames group's experimental setup includes oven attachments that allow them to co-deposit refractory materials along with the more volatiles starting gases.

We are particularly interested in the noble gas trapping properties of residues of ices that have been seeded with PAHs, since large planar PAHs in the resulting refractory residues may provide excellent "cages" for the trapping of noble gases.

We therefore made preliminary investigations into the possibility that noble gases are incorporated into the complex refractory organics produced by UV photolysis of interstellar ice analogs. The results were intriguing enough to suggest that this might be an important process, although they were not definitive. This preliminary work has served as the basis for a full proposal to the Origins of Solar Systems program by T. Swindle, to continue the collaboration with the Ames group.

## Experiments conducted under Joint Research Interchange

We have analyzed residues from two preliminary synthesis experiments, as well as a total of five control samples, under this NASA Joint Research Interchange with Sandford and Allamandola's group at NASA/Ames. In the first experiment, samples of Ni foil were attached on three sides of a rotatable cold head cooled to 10 K. One foil received successive depositions of a mixture of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ ,  $\text{NH}_3$ , and noble gases. Each layer was UV photolyzed with a hydrogen lamp from approximately 10 hours before the next layer was deposited. Another foil was irradiated with UV at each step, but was never directly exposed to the ice + noble gas mixture. A third foil had the ice + noble gas mixture deposited on it, but was never irradiated. The second experiment was identical, except that the sample mixture that was sprayed at the cold foils also included pyrene butyric acid, a four-ring PAH with an alkane group attached, which seemed like a likely candidate for developing linked PAHs in the final room temperature residue. In addition, a sample of foil was handled in the same manner as the others, except that it was never loaded into the sample chamber. The samples foils were then shipped to Arizona, loaded into the extraction line of the noble gas mass spectrometer, baked overnight to about 200°C to remove adsorbed gases (we recognize that this might also degas some of the residue, but if it does, that portion was of limited interest to us anyway), and then dropped into the Ta crucible for

heating. Gases were extracted in two steps, one at about 1000°C and one at about 1500°C.

Results for Kr and Xe in the low-temperature extractions are given in Table 1 (high-temperature extractions released far less gas than the low-temperature extractions, typically within the range that might be expected for blanks). For the first experiment, the mass of the residue was estimated from the yield of other, similar, experiments. The Ames group has less experience with PAH-seeded experiments (they are just beginning to study these mixtures), so the estimate of the mass is much less constrained for the second experiment. A lower limit (0.35mg) is obtained by assuming that none of the PAHs survived in the residue. An upper limit (34 mg) is obtained by assuming that all of the PAHs survived. Later experiments done at Ames using infrared spectroscopy suggest showed that the lower number is likely to be closest to the truth, because the PAHs, while not readily attacked by UV itself, are apparently readily attacked by the O generated in the ice matrix by the UV irradiation.

Several things are immediately apparent. Most importantly, we did trap significant amounts of Kr and Xe in the residues. Indeed, in several cases the concentrations of trapped gases approaches that seen in meteorites. However, the details are not what we would have expected. First, the highest amount of Xe trapped was in the first (no PAH) experiment. Second, the foils that were irradiated, but not directly exposed to the spray of ice plus noble gases, trapped amounts comparable to the fully-prepared samples.

There are possible reasonable explanations for each of these puzzling phenomena, which could be tested with the more detailed experiments suggested in the followup NASA proposal.

First, the subsequent discovery that the UV irradiation of the ice apparently destroys the PAHs makes it less surprising that the sample that started with PAHs is no more efficient at trapping noble gases than the sample that started without. For our purposes, it may be that a much shorter irradiation might retain more of the PAH-like structures, leading to more efficient trapping of noble gases. Since the UV exposure in these preliminary experiments was near the upper limit of what might be reasonably expected in the interstellar medium, a considerably shorter irradiation might be more physically reasonable. Shorter irradiations should result in the destruction of fewer PAHs and may lead to greater gas trapping efficiencies. Another possibility has to do with the effects of oxygen. Because we were concerned that the residue might be destroyed by oxidation, the first set of samples was

TABLE 1: Kr AND Xe IN ICE RESIDUES AND CONTROLS

Experiment	Sample description	<sup>84</sup> Kr (10 <sup>-9</sup> cm <sup>3</sup> STP/gm)	<sup>132</sup> Xe (10 <sup>-9</sup> cm <sup>3</sup> STP/gm)
1	Sample only	1.8	0.35
	UV only	9.4	12
	Sample + UV	9.1	5.4
2	Blank	.001-1.1	.002-0.2
	Sample only	<0.3	<0.2
	UV only	0.8-74	0.01-1.1
	Sample+UV	1.0-92	0.04-3.7

loaded into a vial that had been purged with dry nitrogen, and the vial was not opened until the samples were loaded into the extraction line, at which time all procedures were done in a glove bag filled with dry nitrogen. For the second sample, a vacuum accident in the noble gas mass spectrometer extraction line caused the foils to be exposed to ambient atmosphere for several hours during repairs. We could test the effects of oxygen in the atmosphere (preliminary experiments by the Ames group seemed to show that the effects of oxygen are negligible), but we could also simply keep as many procedures in dry nitrogen atmospheres as possible.

The fact that the foils that were not directly exposed to the ice+noble gas mixtures also trapped significant amounts of gases suggests that some of the noble gases, and perhaps the ices as well, managed to migrate around the cold head and become fixed through the UV irradiation. Again, the cause of this could be tested by doing additional control experiments, for example, an experiment where none of the ice mixture is ever injected into the sample chamber, but noble gases are, and the UV irradiations are performed as normal, an experiment where UV irradiation is carried out with no sample materials of any type, etc.

There are three other aspects of the data that are worth mentioning, and that would be pursued in further work.

First, the residues apparently trapped at least as much Kr as Xe in most cases. Since the original ice mixture had Kr:Xe = 1:1, this suggests comparable trapping efficiencies, unlike chondritic noble gases. Ar was contained in the ice mixture as well, but was not abundant enough for us to have a chance of detecting it at the level at which Kr and Xe were incorporated. In future experiments, we would use different mixes of noble gases, and different ice/noble gas ratios to better constrain relative trapping efficiencies, and to more realistically match the relative and absolute abundances of the noble gases in the starting materials. Since the make up of ices in interstellar clouds vary to some extent (cf. Allamandola and Sandford, 1988), these future experiments could examine an appropriate range of compositions of the non-noble gas starting components as well.

Second, our preliminary experiments did not seem to produce as much isotopic fractionation as Nichols et al. (1992). Our isotopic measurements are not as precise as theirs, because our samples trapped less total Kr and Xe, but none of the samples show isotopic fractionation of either Kr or Xe at  $>1.1\sigma$  level (in some cases, the uncertainties were as small as 0.2-0.3%/amu). By way of comparison, Nichols et al. (1992) measured isotopic fractionations of 0.1-0.4%/amu for Xe and 0.4-1.3%/amu for Kr in their silicate smokes. Although we are not sure of the reason for the difference, if the lack of isotopic fractionation holds up, it suggests that the ice residues might provide a more promising explanation for chondritic noble gases, which show little or no fractionation relative to solar noble gases.

Finally, in our two preliminary experiments we only extracted gas in two temperature steps. In at least some future samples, we will use more steps to better constrain the thermal release properties of the trapped gases.

Our primary goal in all of the experiments in this Joint Research Interchange, and in the followup proposal, is to see if the production of these materials can reproduce both the required absolute abundances of noble gases and the elemental fractionations observed in the chondritic component of meteoritic noble gases, as well as the lack of isotopic fractionation. Even if we fail to exactly reproduce the chondritic component of meteoritic noble gases in later experiments, the results should be two valuable for two reasons. First, understanding the behavior of noble gases in the presence of carbonaceous materials with a variety of structures should make it possible to suggest other scenarios (e.g., combinations of interstellar and nebular

processes) that might work better. In addition, the fact that the procedures that the Ames lab is using reproduce so many features of the interstellar medium suggests that these might be processes that are occurring in nature, whether or not the material survives intact to be incorporated into meteorites. In any case, the preliminary work reported on here suggests that the carbonaceous residues of icy grains are indeed a possible source for the enigmatic chondritic noble gases.

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